Development and Application of Numerical Cluster-Integral Methods to the Description of Inhomogeneous Systems

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Many statistical mechanical theories are formulated in terms of cluster integrals, which represent integrals of the positions of molecules over space, with an integrand that depends on the intermolecular potential. Usually the cluster expansion representations are used in the construction of theories, rather than ends in themselves. However it is possible to compute cluster integrals numerically, and this can be viewed as a treatment for a variety of systems that is rigorously connected to the molecular behavior. In this presentation we consider such approaches in the context of inhomogeneous systems. Bellemanns in 1961 formulated a cluster-integral treatment for inhomogeneous systems. His development was suitable for hard-walled systems only, and was constructed only to third order in the density or activity. Subsequently the approach was extended to other types of external fields by Stecki and Sokolowski. In this work we examine this formalism, extending it to higher orders while retaining its suitability for general external fields. We apply the Mayer-sampling Monte Carlo (MSMC) method to calculate the necessary cluster integrals. MSMC is a general technique for computing configurational integrals, using ideas from free-energy calculations. We consider its use in computing distribution functions for inhomogeneous systems, as well for evaluation of interfacial properties such as the surface tension.